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MICROMEDIA

PRELIMINARY INVESTIGATION OF THE MICROFILTRATION OF OIL SANDS TAILINGS POND SLUDGE

by

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ABSTRACT

Oil sands tailings pond sludge was processed by membrane microfiltration to assess a process for dewatering sludge. Raw and deoiled sludges from the Syncrude tailings ponds were prepared by the Alberta Research Council by using a laboratory bench-scale model of a proposed commercial process. Encouraging results were obtained with the raw sludge in static microfiltration although the bitumen adhered to the polymeric parts of the progressing cavity pump in the cross flow system. The deoiled sludge did not have the same problem, and cross flow microfiltration results were obtained. The permeate was free of oil and visible solids and had very low turbidity. The permeation rates were between 0.5 to 2.0 $m^3/m^2/day$ at less than 100 kPa operating pressure. There was a substantial reduction of the permeation rate that was caused by selectively removing water and leaving concentrated slurry at the membrane surface (gel limited permeation) and the optimal pressure may have been as low as 50 kPa. These results demonstrate the technical feasibility of microfiltration and provide a basis for its economic assessment.

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INTRODUCTION

Oil sands mining and extraction produce a large amount of tailings. These tailings are settled in ponds to give clarified water and sludge. The sludge residues appear to be very stable and consist of a stable oil-in-water (o/w) emulsion with low levels of heavy oil/bitumen and with very high solids contents, approximately 25% by weight. If residual water and bitumen could be removed from the sludge along with the natural surfactants that support the emulsion, the solids could settle. This would permit the use of recovered sludge as an engineering material to fill the quarry created by oil sands mining. The recovered bitumen and water could benefit the oil sands refiner, and an adequate engineering material would reduce the cost of backfilling the oil sand quarries (1).

This work reports the use of microfiltration to dewater both the raw and deoiled sludge. Microfiltration is the use of large pore membranes with nominal pore diameters of several microns to separate solids from liquids. Static microfiltration experiments were performed with both the raw and deoiled sludge. The deoiled sludge is easier to handle, and crossflow microfiltration experiments were performed to determine the technical viability of dewatering in simulated commercial apparatus. Commercial processes that use microfiltration membranes are quite common, and membrane modules are available in many porosities and configurations including modules that can be backwashed in place. It is anticipated that the implementation of a microfiltration process for dewatering deoiled tailings pond sludge would not require excursions from existing microfiltration operating conditions.

EXPERIMENTAL

The tailings pond sludge samples were supplied by Alberta Research Council, Edmonton, Alberta in polyethylene containers. Partial settling of the raw sludge was evident after shipping and storage. After opening, the samples were kept at room temperature and were stirred well prior to use. The gray-brown raw sludge was very viscous with traces of oil and bitumen. The muddy Brown deoiled sludge was much more fluid. Air flotation was used to remove bitumen from the deoiled sludge after it had been diluted with water. The additional water improved the fluidity of the sludge and no bitumen was evident. The deoiled sludge was prepared at the Alberta Research Council by using a bench scale flotation model of a proposed process for bitumen recovery from the sludge.

The static cell used for microfiltration of the raw sludge is shown in Fig. 1. A high pressure filter cell, which was built in-house, was utilized with a 90 mm diameter Pall nylon 6,6 (Ultipor) membrane of 0.1 μm nominal pore size. The effective surface area of the membrane was 40.7 cm^2. Raw sludge was poured into the cell, then closed off from the atmosphere. To force liquid through the membrane, nitrogen gas

was applied under pressure. The permeate was collected in 25 mL portions in small Erlenmeyer beakers to reduce evaporation. The experiment was continued until the permeate tube from the static cell showed evidence of gas escaping or the permeation rate became very low. Typically, this left a solid "cake" on top of the membrane that retained the clays and the residual bitumen. The exact volume of the permeate was determined and the recovery of water was calculated by Eq. 1.

$$\text{Recovery \%} = \frac{\text{(volume of permeate)}}{\text{(volume of original sample)}} \qquad (1)$$

The water remaining in the retentate on the high pressure side of the membrane was determined to be the weight difference after drying at 110°C for 24 h.

The cross flow microfiltration (MF) system consisted of a progressing cavity pump (Robbins and Myers Model SSF/CAA), temperature controlling heat exchanger, ultrafiltration cell (Zenon Environmental Inc.), pressure indicator, temperature indicator, and pressure controller. A schematic is shown in Fig. 2. The ultrafiltration cell was not modified for use in the microfiltration system. It is a thin channel design with parallel flow across the surface of the membrane with a clearance of 1.5 mm, and an effective membrane surface area of 56.4 cm^2. The nature of the membranes (90 mm discs) required taping two membranes together with waterproof tape, and the effective membrane area was reduced. The experiment was performed by filling the pump's reservoir with the deoiled sludge, and pumping the sludge across the membrane surface in a cross flow pattern. The retentate was returned to the pump's reservoir. The membrane permeate was collected, and the permeation rate was determined with respect to pressure and circulation rate. The volumetric recovery was calculated by Eq. 2.

$$\text{Cross flow recovery \%} = \left[1 - \frac{\text{(current reservoir volume)}}{\text{(original volume)}}\right] \times 100\% \qquad (2)$$

Both the raw and deoiled sludge permeates were analyzed for their pH and metals content by inductively coupled plasma (ICP). A sample of the raw sludge permeate was titrated with 0.0550 N HCl (potentiometric titration) to determine the presence of weak acids. The pH meter used was an Accumet model 420 digital (Fisher Scientific) with a combination electrode Ag/AgCl reference (Canadawide Scientific). A model DRT 100 (HF Instruments) was used for turbidity measurement and the conductivity was measured by a YSI model 32 with a conductance cell constant of K = 100/m (Yellow Springs Instrument).

Water content was determined by measuring the weight loss at 110°C for 5 h, and ignoring the effects of volatile bitumen. The solids content was determined by measuring the

weight loss at 500°C overnight. The same titration for the permeate was performed on the sludge and the retentate cake. Sedimentation experiments were performed on the retentate and sludge samples after acidification by placing approximately 40 mL in a 50 mL graduated cylinder, and recording the descent of the sludge front with time.

RESULTS AND DISCUSSION

SLUDGE CHARACTERIZATION

The exact density of the raw sludge was difficult to determine because of the opacity of the slurry. The density was determined to be between 1.17 and 1.25 g/mL. The raw sludge was approximately 71.5 wt% water (evaporation at 110°C) with 23.5% clay (residue at 500°C) The difference (5.5%) was assumed to be bitumen and water of hydration for the clay. The deoiled sludge contained 12.6% solids (residue at 110°C), approximately 0.3% bitumen (2) and had a density of 1.12 g/mL and pH of 8.22.

STATIC MICROFILTRATION

The experiments on the raw sludge were used to determine the nature of the surfactants that stabilized the o/w emulsion and to determine the ion content of the water as shown in Table 1 compared with distilled water. The flotation deoiling process uses deionized water to dilute the raw sludge in an approximate 1:1 ratio and the effect of dilution is apparent in the results of Table 1. The nitrogen gas pressure required for initial permeation was 0.6 MPa wheras that required to complete the permeation experiment was between 3 and 4 MPa, for a slurry loading of 3.6 mL/cm^2 of membrane. The static cells were operated as "dead-end" filters and a typical experiment would require 48 to 96 h to produce 200 mL of permeate from a 300 mL batch sample.

A permeate sample was collected and back titrated with HCl to determine the presence of weak acids as observed in other work with natural surfactants in oily waters and oilfield produced waters of Western Canada (3). The titration curve is shown in Fig. 3 along with raw sludge and 500°C clay. There is evidence of weak acid in the permeate samples and its presence in the raw sludge is masked by the buffering effect of the clay. This is in agreement with the results of acidifying oilfield produced water and the subsequent destabilizing of the emulsion (3,4).

Settling experiments were performed by rediluting the retentate of the raw sludge with deionized water to determine whether sufficient surfactant had been removed. Up to 6 washings of 150 mL of distilled water each were performed. No visible settling was observed. When the raw sludge was acidified to pH 2, approximately 20% free water was observed after one week. This suggests that if the natural surfactants are a significant factor in the stabilization of the sludge,

insufficient amounts are removed from the sludge even after multiple washings.

CROSS FLOW MICROFILTRATION

When the raw sludge was processed by the progressing cavity pump, the plastic stator (Viton material) was immediately coated with the bitumen. This coating occurred to such an extent that the pump was no longer able to function and had to be disassembled and cleaned. From this result, it appears bitumen is selectively adsorbed onto fluoroelastomers such as Viton, and that this may be a possible method for the removal of bitumen from raw sludge. However, for the purposes of this study, raw sludge was not considered for further cross flow MF experiments because of incompatibility with the pump.

Deoiled sludge was entirely amenable to processing in the cross flow MF apparatus, and no problems of bitumen adsorption onto the pump's stator were observed. For these experiments, the temperature of the sludge was held at 40°C and the circulation rate was 4.38 L/min. The Reynolds number for the membrane cell was determined by

$$Re = D V \rho / \mu \qquad (3)$$

where D is a characteristic size dimension, V is the fluid velocity, ρ is the fluid density, and μ is the fluid viscosity. For this case, the characteristic dimension was taken to be the hydraulic diameter defined as

$$D = 2ab/(a+b) \qquad (4)$$

where a is the height of the channel in the membrane holder, 1.5×10^{-3}m, and b is the width of the channel, 4.91×10^{-2} m. With these dimensions, the hydraulic diameter is 2.91×10^{-3}m. For ease of calculation, the ratio of density to viscosity was assumed to be the same as pure water at 40°C, 1.52×10^{4} s/m^{-2}. The fluid velocity was taken to be the circulation rate through the channel divided by the available flow area, calculated to be 1.0 m/s. This gives a Reynolds number of 4400, in the lower level of the turbulent flow regime.

Three membranes were tested and their permeation rates at different operating pressures are shown in Table 2. These results are for the deoiled sludge with only negligible water removal, since the permeate was recycled to the reservoir. These results indicate a very large difference in pressure requirement to operate the static microfiltration (in excess of 3 MPa) compared to the cross flow apparatus (less than 1 MPa) for the same membrane even at minimal recovery levels. The formation of a cake on the high pressure side of the membrane must be avoided if high permeation rates are desired. Visible cake is not formed in the cross flow arrangement. As well, the operating pressure for the cross flow experiments show that for

higher pressures (in the 500 and 1000 kPa range) the permeation rates do not improve.

Another consideration is the membrane type. The cellulose nitrate membrane failed after a short term of use, though this may have been because it is fabricated without an integral support, unlike the nylon membranes. Until the cellulose nitrate membrane is well wetted by water, it remains very brittle and is difficult to handle. Since this membrane apparatus required the taping of two 90 mm membranes together and in the dry state to accommodate the tape's adhesive, it is possible that a crack or weakening of the membrane may have occurred. The poor reliability of the cellulose nitrate membranes available for study in this work precluded further investigation.

The nylon 6,6 membranes used in this work were developed for highly reliable MF in critical applications such as solids removal from liquid chromatography solvents and for the preparation of extreme purity water. They consist of two pieces of membrane bonded to a polyester support to reduce the possibility of membrane failure. They have lower permeation rates than expected for commercial cross flow MF membranes that are designed for large scale separation processes (5). From the results of Table 2, there does not appear to be an advantage in operation at pressures in excess of 100 kPa, in terms of permeation rate. As well there was no evidence of visible differences in quality of the permeates for any of the membranes. The permeates were clear and free of visible solids and bitumen. Since the permeation rates of the membranes were independent of pore size, the 0.04 μm nylon 6,6 membrane was chosen for further study.

The permeation rate of the 0.04 μm nylon membrane was measured as a function of pressure and volumetric recovery as shown in Table 3 for two experiments. Because of the limited amount of sample available, the volumetric recovery was restricted by the volume of liquid for the operation of the pump. As well, the second experiment was performed with reconstituted sludge, obtained by mixing the entire permeate of the first experiment with the retentate. The second experiment was of interest to determine whether there was any significant amount of fouling after operation at high recovery. The losses caused by evaporation of the feed solution at 40°C and handling/sampling losses prevented operation at a higher level of recovery than 48% in the second experiment. From the permeation rates shown in Table 3, it is apparent that there is no decrease in permeation rate as a function of the level of recovery.

As well, the advantage of operating at the higher pressure of 100 kPa in terms of the permeation rate does not appear to be significant. This suggests that despite the turbulence of the cross flow MF apparatus there is still a "gel" limitation effect on the permeation presumably caused by the relatively high solids loading at the surface of the membrane. This gel formation is caused by the removal of water from the region of the membrane surface without sufficient opportunity for the

concentrated (partly dewatered) slurry to diffuse into the bulk of the solution. An indication of gel formation is obtained when a linear increase in permeation rate is not obtained for an increase of pressure. Since it is caused by forcing too much water to leave the slurry before the concentrated layer on the surface of the membrane can be diluted with fresh slurry, lower operating pressures would reduce the stress of removing water, and the membranes would be considered to be more efficient. The increase in permeation rate for the second experiment is possibly caused by denaturing the original sample either by the removal of the water and other components or by the temperature of the feed reservoir.

The appearance of the permeate was clear and free of visible oil and solids. Unlike the results of the static MF experiments, the permeate was crystal clear, and did not have the tinge of yellow associated with the static cell permeates. The yellow colour has also been associated with the permeates from produced water for much smaller pore size membranes than those used in this work, and its absence in the deoiled sludge indicates the natural surfactants and other small organic solutes have been removed by the flotation of the bitumen during the deoiling.

CONCLUSIONS

Static cell MF can be used to produce both a solid cake and a solid and bitumen free water permeate from raw and deoiled sludge. This can be used to assist in the assessment of the water chemistry of the tailings ponds from which the sludge was taken. The raw sludge could not be processed in the cross flow MF apparatus because of incompatibility with the pump. The deoiled sludge was able to be processed by cross flow MF and gave very high permeation rates at low operating pressures, up to the maximum level of recovery as limited by the sample volume. The quality of the permeate appears to be superior to the static MF experiments with the raw sludge, but this may be a function of the deoiling process.

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REFERENCES

1. St. Denis, C.E.and Kessick, M.A. "Recovery of residual bitumen from oil sand sludges", Can J Chem Eng 60:675, 1982.

2. Schutte, R. Syncrude Research, private communication, 1987.

3. Coulombe, S., Farnand, B.A. and Sawatzky, H. "Characterization of surfactants isolated by ultrafiltration

from enhanced oil recovery oil-in-water emulsions", Division Report, ERP/ERL 86-88(J), CANMET,Energy, Mines and Resources Canada.

4. Farnand, J.R. "The treatment of heavy oil emulsions with short chain polar additives", NRC Canada Report, Chem.Div. No. C1090-81S, Dec. 1981.

5. Pall Corporation "The Pall Ultipor N_{66} membrane filter guide", Brochure NM 900 b, 1983.

Table 1 - Properties of static cell permeates[a]

Sludge sample	pH	Cond mS	Turb NTU	Ion concentration, mg/L[b] Na	B	Ca	Mg	Si	SO_4
Raw	8.5	1.568	1.3	466	2.2	4.2	2.4	6.0	5.0
Deoiled	8.0	0.701	0.3	163	1.7	0.7	0.5	12	n/a
Water[c]	6.8	0.0002	0.1	n/a	n/a	n/a	n/a	n/a	n/a

[a] Ambient temperature
[b] Analysis by ICP. P, Mn, Fe, Mo, Sr, Ba all less than 0.5 mg/L
[c] Distilled water

Table 2 - Cross flow microfiltration permeation rates for deoiled sludge[a]

Run No.	Membrane	Nominal pore size μm	Operating pressure kPa	Permeation rate mL/min.
1	Nylon 6,6[b]	0.1	500	1.8
			1000	2.1
			250	0.7
2	Cellulose nitrate[c]	0.01	50	2.1
			100	2.4
			70	2.5
			50	1.8
			70	2.4
			100	4.0[d]
3	Nylon 6,6	0.04	50	3.4
			100	3.5
4	Nylon 6,6	0.1	50	2.1
			100	2.3
5	Nylon 6,6	0.04	50	2.2
			100	2.8

[a] 4380 mL/min circulation rate, 40°C operation, 0% water recovery, 56.4 cm² effective membrane surface area
[b] Manufactured by Pall Ultipor
[c] Manufactured by Sartorius
[d] Followed by membrane failure

Table 3 - Permeation rate with water recovery[a]

Run No.	Volumetric recovery %	Operating pressure kPa	Average permeation rate mL/min
1	0	50	2.2
		100	2.8
	21.7	50	3.5
		100	4.2
	21.7[b]	50	4.6
		100	4.8
	43.5	50	7.6
		100	6.7
	65.2	50	4.9
		100	6.0
2[c]	0	50	8.5
		100	9.3
	16.3	50	7.4
		100	7.9
	32.6	50	6.0
		100	7.4
	48.9	50	4.7
		100	5.3

[a] Pall Ultipor Nylon 6,6 microfiltration membrane, 0.04 m nominal pore size, 4.38 L/min circulation rate, 40°C operating temperature, deoiled sludge, 56.4 cm^2 effective membrane surface area

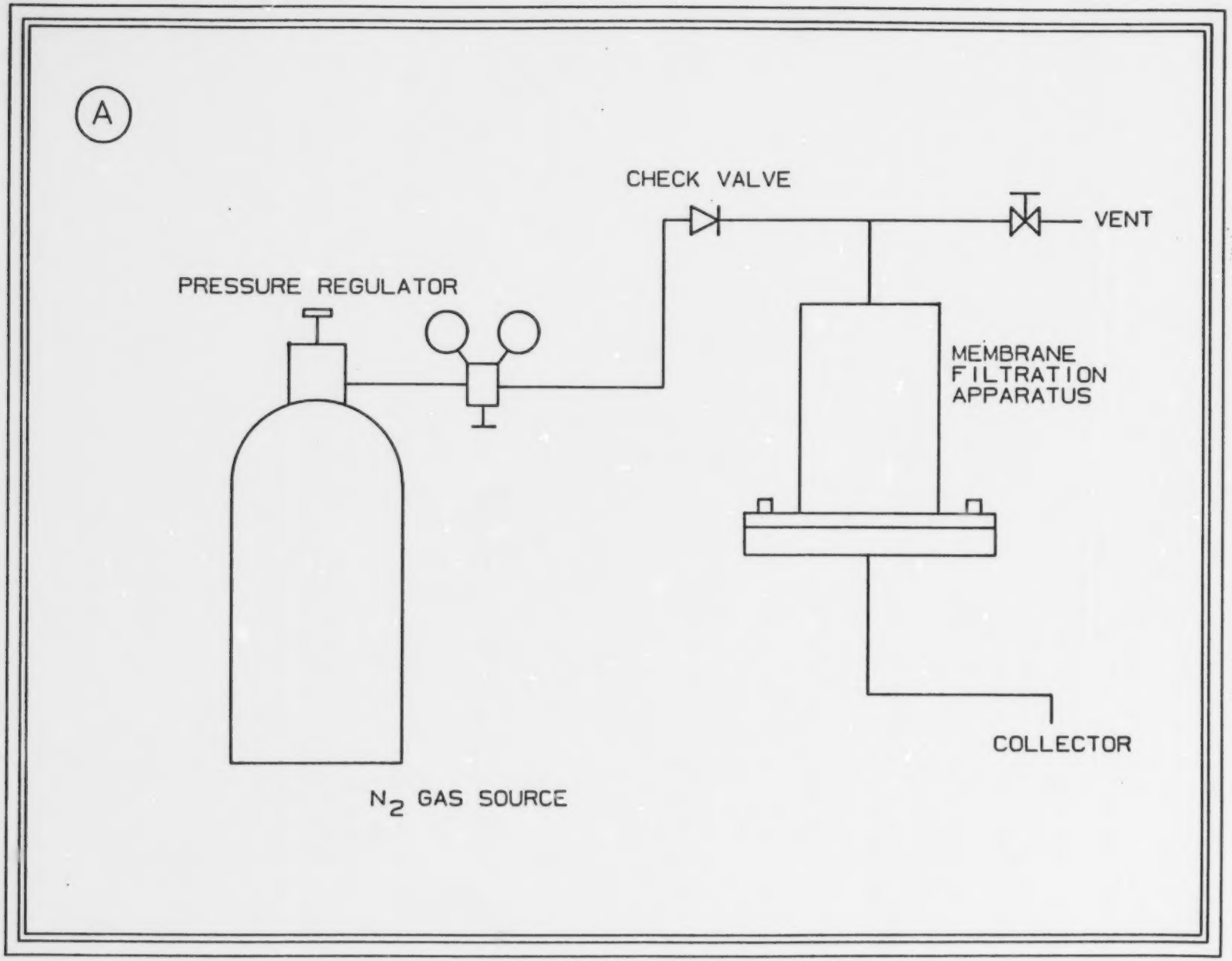
[b] Repeated experiment after the system was left overnight at ambient temperature

[c] Reconstituted sludge from Run No. 1

Figure 1 A. Schematic of static microfiltration equipment
B. Detailed schematic of static cell

Figure 2 Schematic of cross flow microfiltration equipment

Figure 3 Titration curves for raw sludge components
25.00 mL permeate
1.0044 g 500°C clay in 25.0 mL distilled water
25.0 mL raw tailings pond sludge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FILTRATION
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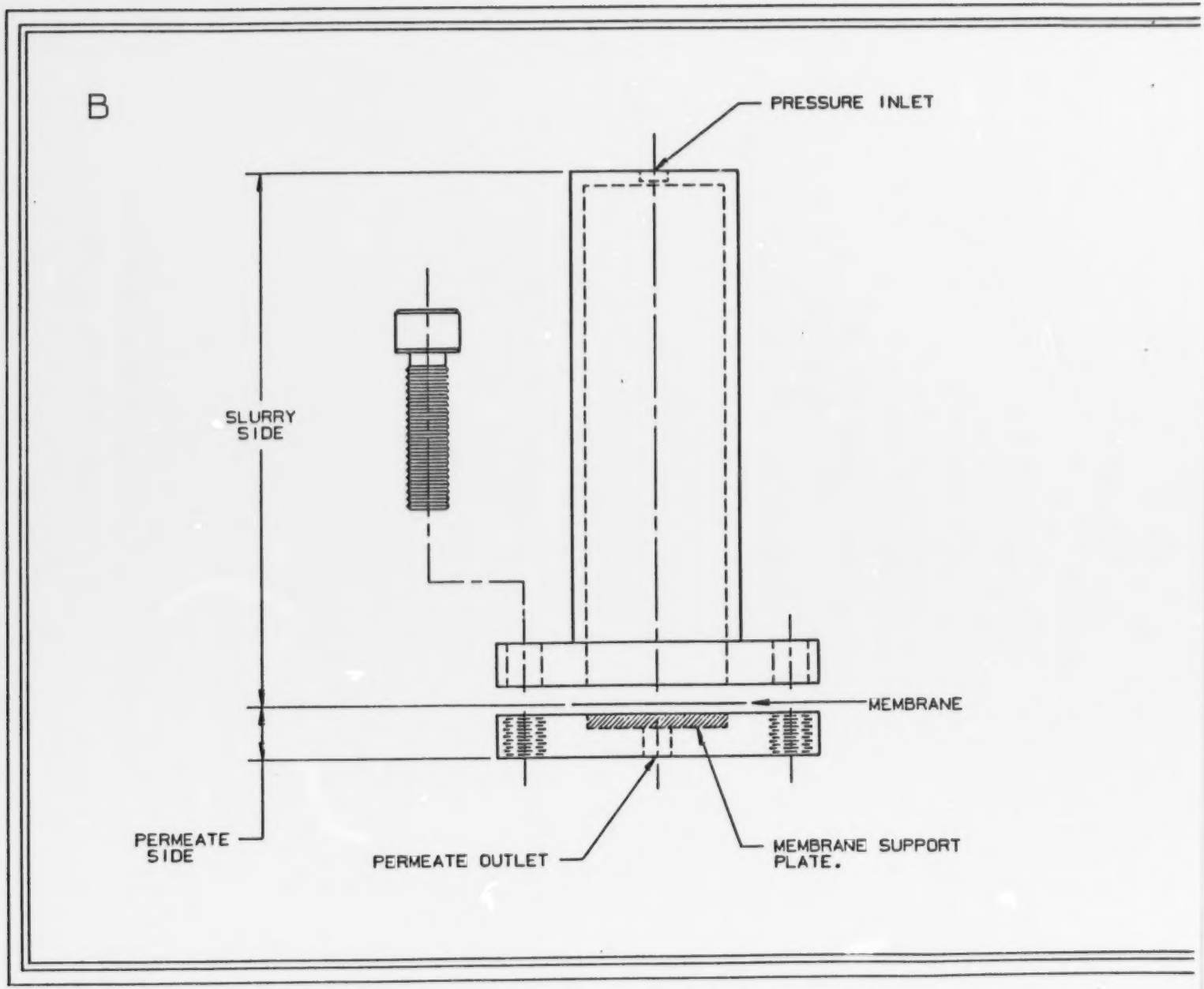
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PERMEATE SIDE
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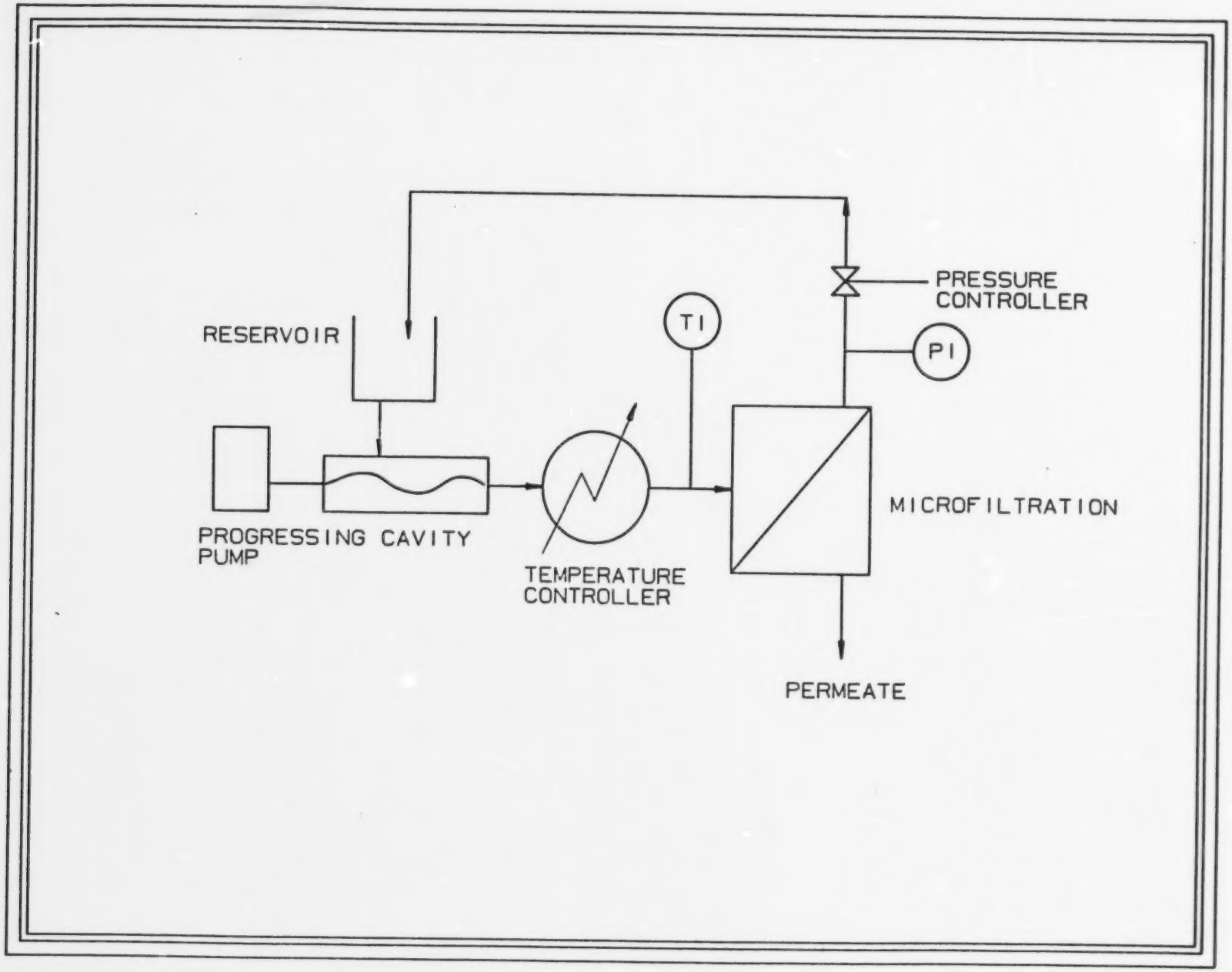
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TI
PRESSURE CONTROLLER
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PROGRESSING CAVITY PUMP
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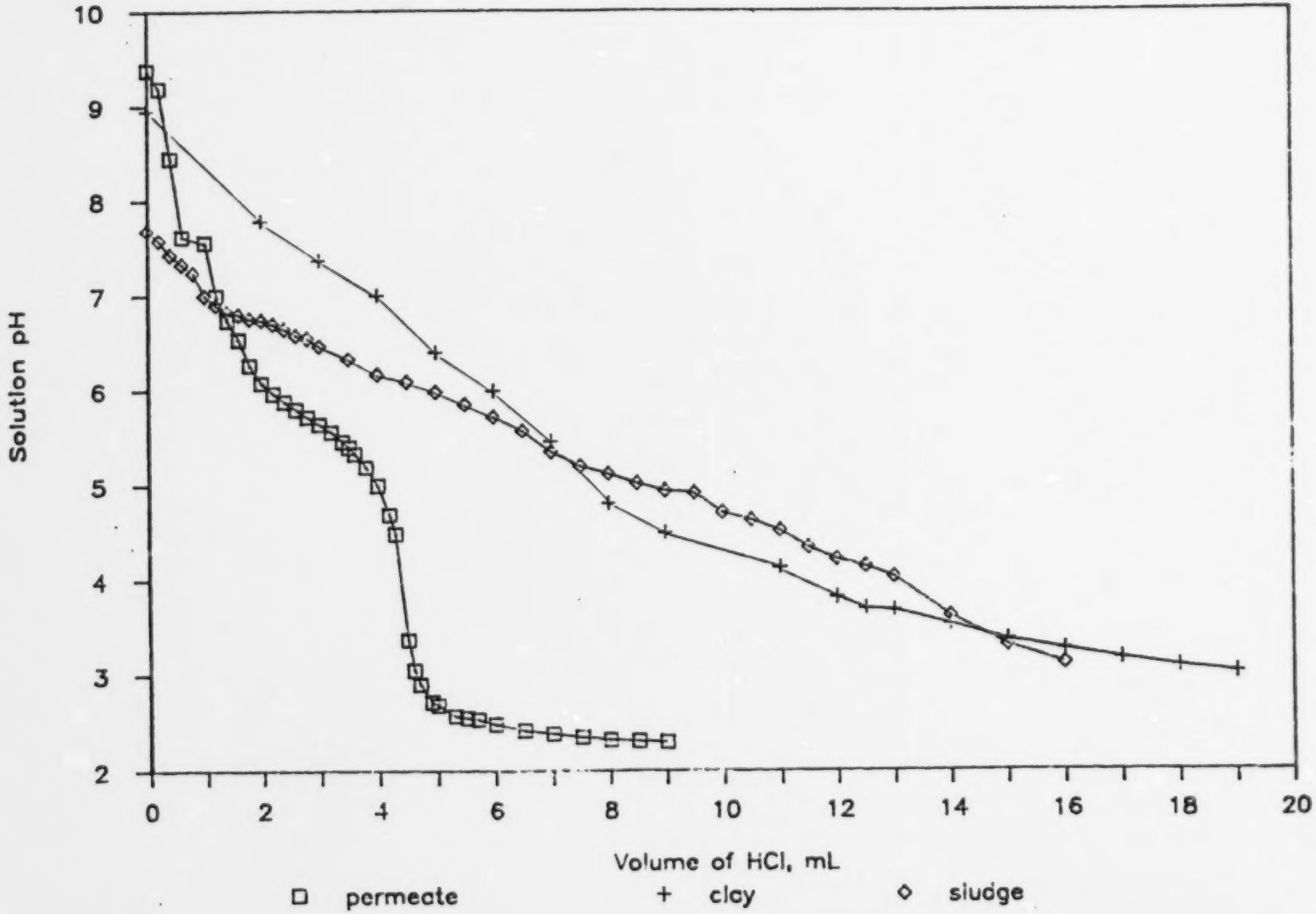
PERMEATE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8
7
6
5
4
3
2
0
2
4
6
8
10
12
14
16
18
20
Volume of HCl, mL
permeate
clay
sludge